Resonance-Assisted O–H···O Hydrogen Bonding: Its Role in the Crystalline Self-Recognition of β-Diketone Enols and Its Structural and IR Characterization

Valerio Bertolasi, Paola Gilli, Valeria Ferretti and Gastone Gilli*

This paper is dedicated to the memory of Prof. Margaret C. Etter, University of Minnesota, who first recognized the importance of β-diketone enols in hydrogen-bonding studies

Abstract: The fact that hydrogen bonding is normally stronger than other nonbonding attractive forces can be exploited for the rational design of molecular crystals with known packing features and specific physical properties (crystal engineering). In the present paper the problem of obtaining homodromous molecular chains controlled by strong O–H···O interactions is investigated, particular attention being paid to *β-chains*, that is, infinite hydrogen-bonded chains of β-diketone enol fragments ···O=C–C=C–OH···, which are linked by stronger-than-usual *resonance-assisted hydrogen bonds (RAHBs)* and are intrinsically interesting as prototypes of a large family of switching proton bistate molecular devices. Accordingly, the crystal and molecular structures of thirteen new compounds containing the 1,3-cyclopentanedione and 1,3-cyclohexanedione fragment (or their heterocyclic analogues) were determined, and most of them were found to give the expected β-chain packing pattern. Comparison with literature data makes it possible to identify seven fundamental β-chain patterns, which can be shown to be selected by reason of the relative encumbrances of the substituents. Furthermore, a general analysis of all functional groups able to form strong O–H···O bonds reveals a semiquantitative correspondence between the O–H···O measurable parameters (O···O, H···O and O–H distances, and $\tilde{\nu}$(O–H) IR stretching frequencies) and the hydrogen bond energy E_{HB}, and a hierarchy of chemical functionalities that are well characterized by limited E_{HB} ranges and that, in decreasing order of energy, can direct the crystal packing process.

Keywords
crystal engineering · diketone enols · hydrogen bonds

Introduction

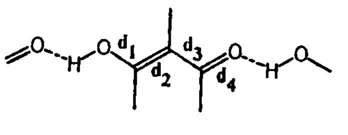
It is hard to exaggerate the role played by hydrogen bonding in molecular recognition phenomena. The autoaggregation of molecules in crystals, in particular, is strongly affected by both number and strength of the hydrogen bonds formed and there can be little doubt that more detailed modelling of hydrogen-bonding interactions could make an important contribution to the rational design of crystals having specific physical properties (crystal engineering).[1a] The simplest and most direct approach to crystal design consists in singling out those molecular fragments which are able to form hydrogen bonds strong enough to overcome the other crystal forces, giving characteristic hydrogen-bonded structures (such as dimers, large rings, chains, helices, etc.) that are retained unaltered in the final crystal architecture. This approach, which is not far from Hartman's PBC (Periodic Bond Chains)[1b] method for the prediction of crystal habits, seems particularly appropriate for the design of crystals containing homodromous chains of molecules linked by a single dominant intermolecular interaction, and the present paper is essentially devoted to establishing whether, and under what conditions, such dominance can be achieved by means of intermolecular O–H···O interactions. It has been recently proposed[2a] that short (strong) O–H···O bonds (say, having O···O distances in the range 2.36–2.65 Å) are caused by an increased $O^{\bullet}-{}^{\bullet}H\cdots{:}O \leftrightarrow O{:}\cdots H^{\bullet}-{}^{\bullet}O$ three-centre–four-electron covalent contribution, which turns out to be possible only in three well-determined chemical situations: i) -O–H···$^{-}$O- or negative-charge-assisted hydrogen bond, (–)CAHB; ii) =O···H^{+}···O=, or positive-charge-assisted hydrogen bond, (+)CAHB; iii) -O–H···O= or resonance-assisted hydrogen bond, RAHB, where the two oxygens are connected by a π-conjugated system.

The potential of CAHB for promotion of crystal chain formation has never been studied in a systematic way, though the role played by (–)CAHB has been pointed out in some instances, such as the chain formation of acidic oxoanions (e.g., ···$^{-}$OP(O)(OH)OH··· chains in KH_2PO_4)[3a,b] or monoacidic bicarboxylic acids (···$^{-}$OOC–$(CH_2)_n$–COOH···).[3c,d] Conversely, it has often been remarked[2b–d] that O–H···O

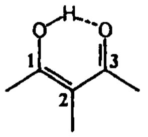
---

[*] Prof. G. Gilli
Department of Chemistry, Università di Ferrara
via Borsari 46, I-44100 Ferrara (Italy)
Fax: Int. code +(532)240-709
e-mail: m38a@icineca.cineca.it
V. Bertolasi, P. Gilli, V. Ferretti
Centro di Strutturistica Diffrattometrica and Dipartimento di Chimica
Università di Ferrara, I-44100 Ferrara (Italy)

bonded chains of neutral entities can be considerably strengthened if advantage is taken of the synergistic mechanism of hydrogen bond strengthening and π-resonance reinforcement typical of RAHB, which may be effective for resonant groups of any length (carboxylic acids, $\cdots O{=}C{-}OH\cdots$; inorganic oxo acids, such as $\cdots O{=}S(O)(OH){-}OH\cdots$ or $\cdots O{=}P(OH)_2{-}OH\cdots$; β-diketone enols, $\cdots O{=}C{-}C{=}C{-}OH\cdots$ (**Ia**); δ-diketone enols $\cdots O{=}C{-}C{=}C{-}C{=}C{-}OH\cdots$; etc.). Moreover, it has been suggested[2d] that crystals containing such *noncharged resonant chains* may have important technological applications, particularly in the field of nonlinear optics;[4] they are in fact potential monodimensional bistate systems of infinite length because of the keto–enol ⇌ enol–keto tautomerism of the chain $\cdots O{=}C(-C{=}C)_n{-}OH\cdots \rightleftharpoons \cdots HO{-}C({=}C{-}C)_n{=}O\cdots$ ($n = 0, 1, 2\ldots$).



Ia



Ib

The present paper reports the crystal and molecular structures of thirteen new β-diketone enols **I** that were expected to form such infinite resonant chains **Ia** (β-chains), and the morphologies of the β-chains obtained are compared with those of other similar crystal structures in an attempt to single out the general rules followed by β-diketone enols during the chain formation process. Subsequently, the hydrogen bond geometries, IR $\tilde{\nu}$(O–H) stretching frequencies and estimated energies obtained for the present compounds are analyzed and compared with those of other classes of O–H···O bonds with the aim of establishing a hierarchy of functional groups able to form stronger-than-usual intermolecular O–H···O bonds potentially able to direct the crystallization process in a predictable way.

Experimental Data: Compounds to be investigated were chosen so as to avoid the formation of the intramolecular O–H···O bond **Ib** which, in the absence of steric hindrance, is favoured by entropic factors.[2d] Since the simplest way is to embed the enolone fragment in a ring, thirteen compounds containing the leitmotiv of 1,3-cyclopentanedione or 1,3-cyclohexanedione (or their heterocyclic analogues) were selected, crystallized from organic solvents, and submitted to crystal structure determination. Crystallographic data and experimental details are given in the Experimental Section and the most relevant hydrogen bond parameters are listed in Tables 1 and 2. Views of the molecules and of their association patterns are shown in Figure 1. Table 1 (first column) reports the hydrogen-bonded structures found: β-chains correspond to structure **Ia**, which is found in compounds **1–5** and **7–10** (Fig. 1); α-dimer and β-dimer indicate the arrangements displayed in structures **13** and **6**, respectively; the term w-chain is used for chains of β-diketone enol fragments intercalated by water molecules. FT-IR spectra of powdered crystals were also recorded with the aim of measuring the ν(O–H) stretching frequencies of the enolic proton; results are shown in Table 1 together with some relevant parameters of the O–H···O bonds formed. Table 2 summarizes the types of hydrogen-bonded chains observed in compounds **1–10** and other β-diketone enols of known molecular structure. All crystal data were retrieved from the Cambridge Structural Database.[5a]

Table 1. Hydrogen bond parameters d(O···O) (Å), α(O–H–O) (Å), Q (Å), λ and $\tilde{\nu}$(OH) (cm^{-1}) for compounds **1–13** and some β-diketone enols from the literature (indicated by their CSD [5a] references). E_{HB} (kcal mol^{-1}) is the hydrogen bond energy according to Lippincott and Schroeder [6]. E.s.d.'s are 0.002–0.004 Å (0.009 Å for **3** and **9**) for d(O···O) and 2–4° for α(O–H–O); numbers in angle brackets ⟨⟩ represent averages.

Compound	HB structure	d(O···O)		α(O–H–O)	Q	λ	$\tilde{\nu}$(OH)	E_{HB}
1	β-chain	⟨2.611⟩		⟨178⟩	⟨0.198⟩	⟨0.81⟩	2690	7.1
2 [a]	β-chain	2.589		178	0.172	0.77	2616	7.9
3	β-chain [b]	2.588			0.102	0.66	2517	–
4	β-chain	2.625		175	0.158	0.75	3000	6.5
5	β-chain [b]	2.604		172	0.157	0.74	2700	7.2
6	β-dimer	⟨2.586⟩			0.00	0.50	2600	–
7 [c]	β-chain	2.600		174	0.156	0.74	2620	7.4
8	β-chain [d]	⟨2.718⟩			⟨0.217⟩	⟨0.84⟩	3174	–
9	β-chain	2.592			0.154	0.74	2627	–
10	β-chain	2.605		163	0.150	0.73	2800	6.3
PROLON [e]	β-chain	2.577		175	0.135	0.71	2560[f]	8.3
FACRIK [g]	β-chain	2.539		169	0.163	0.75	2500[f], 2500	9.7
DETSBR01 [h]	β-chain	2.465		176	0.084	0.63	≈1200 [f]	15.5
DIMEDO [i]	β-chain	2.593		176	0.147	0.73	2500[f], 2500	7.6
JEMRAU [j]	β-chain	2.542			0.145	0.73	2450 [f], 2470	
LASCAC10 [k]	β-chain	⟨2.661⟩		⟨153⟩	⟨0.224⟩	⟨0.85⟩	3030	3.8
	OH···OH	⟨2.629⟩, 2.707, 2.769, 2.786, 2.935			–	–	2736, 3218, 3316, 3411, 3528	
IASCOR10 [l]	β-chain	2.645		151	0.244	0.88	3013	3.8
	OH···OH	2.587, 2.780, 2.829			–	–	2750, 3335, 3484	
13	α-dimer	2.706			0.239	0.87	3270	–
		d(O–H···O$_w$)	d(O$_w$–H···O=)					
11	w-chain	2.570	⟨2.771⟩	⟨173⟩	0.164	0.76	2660, 3360	8.5, 3.1
12	w-chain	2.593	2.791	⟨164⟩	0.212	0.83	2620, 3358, 3492	6.9, 2.4
	w···O=C		2.855		–	–		

[a] Redetermination of the structure of 2-methyl-1,3-cyclohexanedione (PEPHUN) [8a]. [b] Disordered structure. [c] Redetermination of the structure of 2-methyl-1,3-cyclopentanedione (SEFSIF) [8b]. [d] Bifurcated (three-centre) hydrogen bond. [e] Phenylmalondialdehyde [8c]. [f] Refs. [7e–g]. [g] 1,3-Cyclohexanedione [8d]. [h] 1,3-Diethyl-2-thiobarbituric acid [8e]. [i] 5,5-Dimethyl-1,3-cyclohexanedione (dimedone) [8f]. [j] 1,3-Cyclopentanedione [8g]. [k] L-(+)-Ascorbic acid (vitamin C) [8h]. [l] D-Isoascorbic acid [8i].

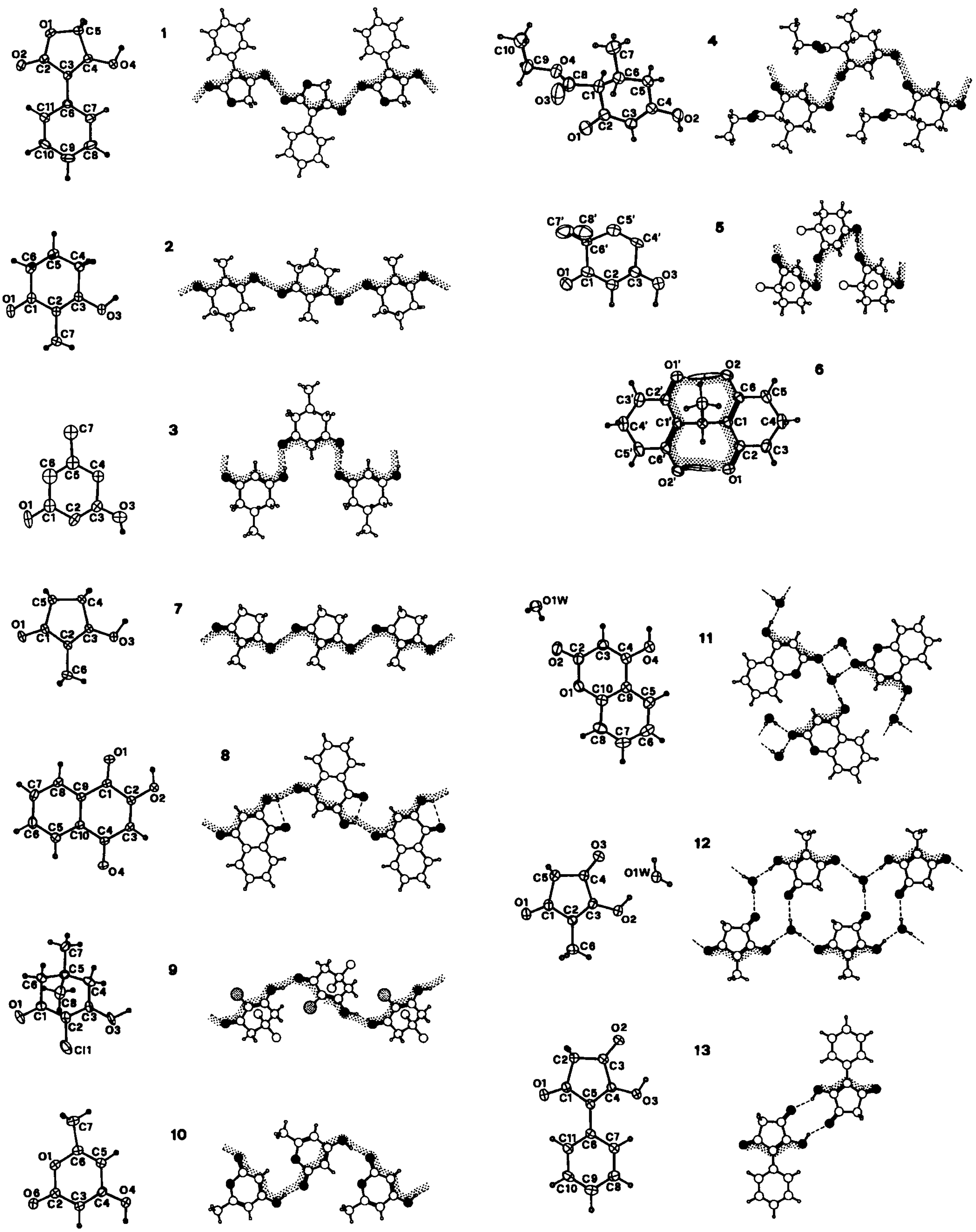


Fig. 1. ORTEP [24d] views of the molecules with thermal ellipsoids at 30% probability and PLUTO [24e] drawings of their hydrogen-bonding patterns for compounds **1**–**13**.

Table 2. Summary of hydrogen-bonded chains observed in crystals of compounds **1**–**10** and of some β-diketone enols from the literature (indicated by their CSD [5a] reference codes). Symbols are explained in the text; ϕ angles in degrees; n-ring = the enolone is part of a n-membered ring; R_2 = substituent in position 2 (see **I**); numbers in angle brackets ⟨⟩ represent averages.

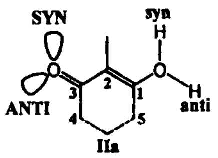
Compound	Chain	ϕ (plane)	ϕ (axis)	n-ring	R_2	Chiral molecule	Space group	Z	Polar chain
Chain type: *ap-anti–ANTI* (**III.1a**)									
1	$t(A-B)$ (*pseudo-g*)	17	⟨14⟩	5	Ph	no	$P\bar{1}$	4	no
2	g	4	8	6	Me	no	$Ibam$	8	no
PROLON	g	4	3	linear	Ph	no	$Pma2_1$	4	no
FACRIK	g	1	4	6	H	no	$P2_1/a$	4	no
Chain type: *ac-anti-ANTI*									
FIVKEA [a]	$t(A-B)$	67	⟨5⟩	5	Ph	yes	$P2_1$	4	yes
Chain type: *ap-syn–SYN* (**III.2a**)									
3	g or 2_1 [b]	5	1	6	H	rac	$Cmc2_1$	4	no
4	2_1	9	22	6	H	rac	$P2_1/c$	4	no
DETSBR01	2_1	16	10	6	H	no	$P2_12_12_1$	4	no
Chain type: *sp/sc-syn–SYN* (**III.2b** and **III.2b′**)									
6	–	44	–	6	CHMe				
FERBUZ [c]	2_1	55	62	6	Ph	no	$C2/c$	8	no
5	2_1	87	47	6	H	no	$P2_12_12_1$	4	no
DIMEDO	2_1	85	49	6	H	no	$P2_1/c$	4	no
BOMYAD01 [d]	$t(A-B)$ (*pseudo*-2_1)	82	⟨52⟩	6	H	rac	$P2_1/c$	8	no
CIHNAI [e]	2_1	76	53	5	R [f]	no	$Pca2_1$	4	yes
Chain type: *ap-syn–ANTI* or *ap-anti–SYN* (**III.3a–b**)									
7	t	0	20	5	Me	no	$C2/m$	4	no
BEWHUG [g]	t	0	21	5	Me	yes	$P2_1$	2	yes
MTETAC02 [h]	t	0	21	5	Me	no	$P2_1/c$	4	no
DMTETA01 [i]	t	0	19	5	Me	no	$P2_1/c$	4	no
IASCOR10	t	0	21	5	OH	yes	$P2_1$	2	no
LASCAC10	$t(A-A)$ $t(B-B)$	0	⟨22⟩	5	OH	yes	$P2_1$	4	no
KECYBU06 [j, k]	t	0	⟨22⟩	4	OH	no	$P2_1/m$	2	no
Chain type (closed ring): *ap-syn–ANTI* (**III.3d**)									
FACROQ [l]	($6/m$)	5	–	6	H	no	–	–	–
Chain type: *sp/sc-syn–ANTI* or *sp/sc-anti–SYN* (**III.3e**)									
8	$t(A-B)$ (*pseudo-g* or 2_1)	4	⟨37⟩	6	H	no	$P\bar{1}$	4	no
9	g	69	37	6	Cl	no	$P2_1/c$	4	no
10	g	20	49	6	H	no	$P2_1/n$	4	no

[a] (5*R*)-2,5-Dihydro-4-hydroxy-5-methyl-3-phenyl-5-prop-1′-enyl-2-oxothiophene [8j]. [b] Disordered structure in $Cmc2_1$ space group. [c] 5-phenylbarbituric acid [8k]. [d] 4-Hydroxybicyclo[3.3.1]non-3-en-2,9-dione [8l]. [e] 7-(5-Hydroxy-3-oxo-2,3-dihydro-4-pyrazolyl)theophylline [8m]. [f] R_2 = 7-Theophyllinyl. [g] (–)-4-Hydroxy-3,5-dimethyl-5-[3-oxo-(*E,E*)-4,6-octadienyl]-2(5*H*)-furanone (vertinolide) [8n]. [h] α-Methyltetronic acid [8o]. [i] DL-α,γ-Dimethyltetronic acid [8p]. [j] Two intercrossed β-chains. [k] 3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid) [8q]. [l] 6:1 1,3-Cyclohexanedione:benzene cyclamer [8d].

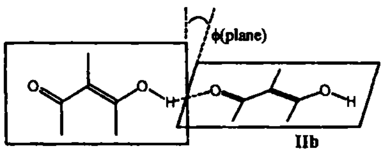
Results and Discussion

β-Chain Morphologies: Out of the thirteen crystal structures determined, nine are found to form β-chains (**1**–**5** and **7**–**10**), one an intramolecular β-dimer (**6**), two β-chains intercalated by water molecules (w-chains; **11** and **12**), and only one a nonresonant hydrogen-bonded dimer (**13**). The crystal packing is thus dominated by RAHB in 10/13 cases, with formation of the expected resonant chain in 9/13 instances.

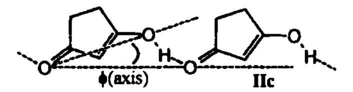
Analysis of β-chain morphologies requires an appropriate nomenclature and this is done by two complementary methods.[2d] The first is crystallographic; the chain symmetry is described by means of the symmetry operation relating adjacent molecules in the chain. Symbols g for glide, 2_1 for binary screw *axis* and t for lattice translation are used; multiple asymmetric units are indicated as A–B, the notation t(A–B) denoting two interlinked molecules that propagate the chain by simple translation; the prefix *pseudo* may be used for approximate (i.e., noncrystallographic) symmetries, for example *pseudo*-2_1. The second system of notation defines the stereochemical chain conformation; it follows the (*syn*/*anti*–*SYN*/*ANTI*) nomenclature (**IIa**) originally proposed by Etter et al.[8d] Of the four possible combinations, two (*syn–ANTI* and *anti–SYN*) give essentially equivalent chains by interconversion through $O-H\cdots O \rightleftharpoons O\cdots H-O$ tautomerism and can therefore be grouped together. Since the global β-chain conformation is also affected by rotation around the intermolecular $C-OH\cdots O{=}C$ connection, the C-O-O-C torsion angles were monitored according to the Klyne–Prelog convention,[5c] in which sp = synperiplanar, sc = synclinal, ac = anticlinal and ap = antiperiplanar for torsion angles in the ranges ±30°, ±(30–90)°, ±(90–150)°, and 150–210°, respectively. Finally, chain morphology is quantified by the values of two angles: ϕ(*plane*) is the angle (**IIb**) between



IIa



IIb



IIc

the least-squares planes through C(1), C(2), C(3), O(1) and O(2) atoms of two adjacent monomers, and $\phi(axis)$ is the angle (**IIc**) between the chain translation axis and the vector connecting O(1) and O(2) within one monomer. Chain-symmetry and chain-conformation descriptors together with $\phi(plane)$ and $\phi(axis)$ values are given in Table 2 for **1**–**10** and 15 other compounds[8c–q] retrieved from CSD[5a] which likewise form β-chains. The table shows that all possible *syn/anti–SYN/ANTI* permutations are actually found. Accordingly, the β-chains display a great variety of forms, their principal common feature being the predominance of globally planar chains ($\phi(plane) \leq 20°$ in 14/24 occurrences). A detailed comparison of the different chains suggests, however, that a rationalization of their morphologies can be achieved on the following grounds:

i) The β-diketone enol fragment **IIa**, as well as its O–H bonds and carbonyl lone pairs, tends to be coplanar by conforming to the trigonal geometry of the sp^2 hybridization.[8d, 9]

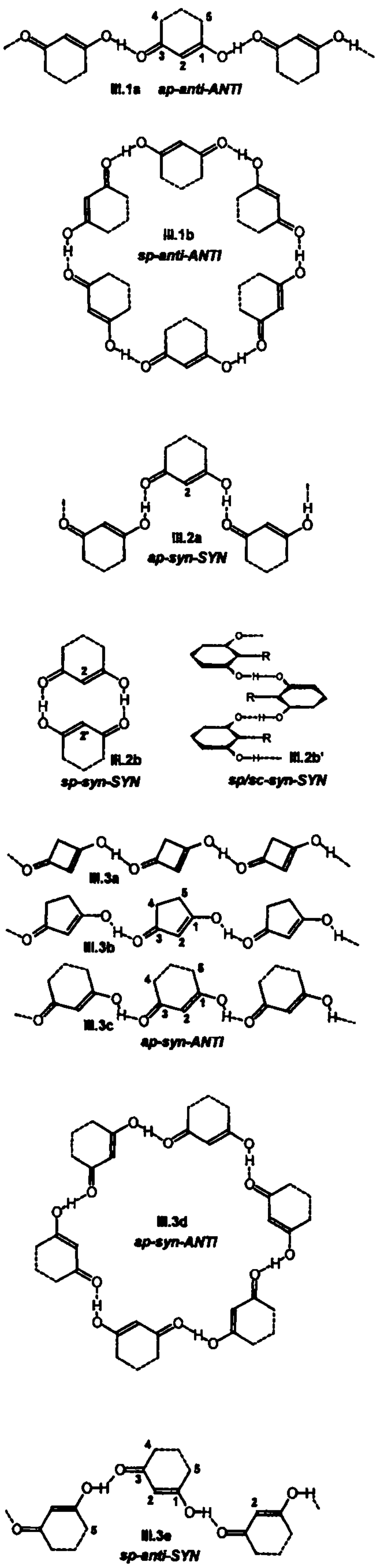
ii) All hydrogen bonds display a tendency to be more linear the shorter they are,[10] but this condition becomes stringent in β-chains where RAHB-shortened O···O distances are mostly in the range 2.46–2.62 Å (Table 1) and the corresponding O–H···O angles must remain confined in the interval 163–180° according to the most accurate statistics published.[10c]

iii) Constraints of chain planarity and H-bond linearity lead to a limited number of predictable planar combinations of β-diketone enol groups, which are illustrated in schemes **III**; they can be divided into *large rings* (**III.1b**, **III.3d**), *spiral helices* of 2_1 symmetry (**III.2b′**) and *flat chains* of *t* (**III.3a–c**), 2_1 (**III.2a**) and *g* (**III.1a**, **III.3e**) symmetry.

iv) The adoption of a particular form from among the different β-chains, as well as their possible deviations from planarity, can generally be related to the comparative encumbrances of substituents located at positions 2, 4 and 5 of **IIa**, as discussed below.

Large rings: Cyclic arrangements (**III.1b**, **III.3d**) should be forbidden because the void at the centre of the ring violates the close-packing rule;[1c] it may be supposed that their realization requires filling that void with a molecule of proper size and shape. Actually, a single case of ring **III.3d** is known to occur (FACROQ in Table 2), in which six cyclohexanedione molecules are arranged, with 6/*m* symmetry, around a central molecule of benzene, the solvent used for crystallization.[8d]

Spiral helices: The dimeric *sp-syn–SYN* arrangement **III.2b** is highly unlikely because of the overlapping of the 2 and 2′ substituents (even if hydrogens), but we have succeeded in obtaining a strained version of it by synthesizing compound **6** (Fig. 1) where 2 and 2′ are covalently bridged. Pattern **III.2b** is, however, important because it can be transformed into a β-chain by imparting opposite inclinations to the two adjacent hydrogen-bonded monomers. The result is the wide *sp/sc-syn–SYN* helix **III.2b′** resembling a spiral staircase of 2_1 symmetry, which can easily accommodate large substituents in 2 and 4 and/or 5 positions and, for this reason, is adopted in a number of cases (FERBUZ, **5**, DIMEDO, BOMYAD01 and CIHNAI in Table 2). In particular, the chain appears to be stabilized by large and flat 2-substituents (phenyl in FERBUZ and 7-theophyllyl in CIHNAI) having the correct shape for improved van der Waals packing efficiency within the spiral. In these chains both $\phi(plane)$ and $\phi(axis)$ angles assume remarkably large values (47–87°), unlike in the other types of chains.



Flat chains: With two exceptions (FIVKEA and **9**), all other chains are essentially planar, with $\phi(plane) \leq 20°$, and display crystallographic or approximate *t*, 2_1 or *g* symmetries. They include:

t-chains: Translational *t*-chains belong to the *ap-syn–ANTI* group **III.3a–c** (or to the equivalent *ap-anti–SYN* group); this association pattern is exhibited by seven compounds (**7**, BEWHUG, MTETAC02, DMTETA01, IASCOR01, LASCAC10 and KECYBU06). They share the common features that the β-diketone enol group is included only in four- or five-membered rings and that the 2-substituent is never bulkier than a methyl group. The angle between the chain and monomer axes, $\phi(axis)$, is remarkably constant at 19–22°, so giving the correct inclination for straightening the $O-H\cdots O$ bond (see **III-3a** and **3b**). Six-membered rings cannot fulfill this last condition because of interatomic repulsions (compare **III.3c** with **III.3a** and **3b**) and, accordingly, cyclohexanedione derivatives are not found to form *t*-chains.

2_1*-chains*: The *ap-syn–SYN* chain **III.2a** of symmetry 2_1 requires that the 2-substituent is no larger than hydrogen, but can accommodate even bulky substituents on the other side of the six-membered ring; it is, in fact, adopted by a small number of cyclohexanedione derivatives having these characteristics (**3**, **4**, DETSBR01).

g-chains: Two different types of *g*-chains are found: *ap-anti–ANTI* (**III.1a**) and *sp-anti–SYN* (**III.3e**). The first can easily accommodate bulky substituents in all 2, 4 and 5 positions and would be expected to occur quite often. In fact, it is observed in a limited number of cases (**1**, **2**, PROLON, FACRIK) with no substituents at all except a 2-phenyl (in **1** and PROLON). A possible explanation is that chains can be stabilized by both the strong $O-H\cdots O$ bonds and an efficient *intrachain* packing of the substituents (as already remarked above for spiral helices) but the latter is ineffective in **III.1a** because adjacent substituents are far away. The pattern *sp-anti–SYN* (**III.3e**) represents the opposing situation of possible intrachain stabilization. The chain is, by itself, rather unstable because of the too small $O-H\cdots O$ angle achievable but could be easily stabilized by attractive 2–5 interactions, which are in fact observed in all compounds adopting this type of chain in the form of the weak $C-H\cdots O$ bonds found in **8** and **10** (Fig. 1) and of a $CH_2\cdots Cl$ contact in **9** (Fig. 1).

The fact that most experimentally observed β-chains can be accounted for on the ground of simple intramolecular factors strongly suggests that the resonant $O-H\cdots O$ bond alone is strong enough to direct the formation of the chain, which is only shaped in a variety of forms by steric factors. However, knowledge of the molecular structure does not necessarily enable correct prediction of the precise β-chain that forms, but can only suggest the probability of formation of any particular one. In this sense, it might be asserted that *cyclopentanediones* having small substituents at position 2 but derivatized in a wide variety of ways at positions 4 and 5 are *likely* to give simple *ap-syn–ANTI* (**III.3b**) *t*-chains, while *cyclohexanediones* substituted at 4 and/or 5 will *probably* give *ap-syn–SYN* (**III.2a**) 2_1-chains or *sp/sc-syn–SYN* (**III.2b′**) spiral helices according to whether they are unsubstituted or substituted by a large and flat group in position 2.

The prediction of the chain type, however, does not tell us how the chains will pack in the final crystal. This problem may be of particular relevance in the planning of noncentrosymmetric crystals where the β-chains are to be disposed along a unique polar axis. A previous study has shown that β-chains assume large dipole moments because of the unidirectional π delocalization along the chain and, accordingly, display a great tendency to antidromous polar pairing.[2d] Only one case of a nonchiral molecule giving polar chains is known (CIHNAI in Table 2) and two cases of chiral ones (FIVKEA and BEWHUG). Though choosing a chiral molecule is one obvious route to achieving chain polarity, this is not always a sufficient condition, as demonstrated by the crystal structures of the chiral compounds MTETAC02 and DMTETA01 (space group $P2_1$) where the β-chains are antidromously related by the 2_1 axis perpendicular to them. At present, only the crystal structure determination of more chiral derivatives is likely to produce a greater insight into the nature of the problem and its solution.

Hydrogen Bond Strength in β-Chains: The relevant hydrogen bond parameters for **1–13** and some other related compounds for which IR data were available (or could be measured) are collected in Table 1. $d(O\cdots O)$ and $\nu(O-H)$ are the most frequently used indicators of hydrogen bond strength. O–H and $H\cdots O$ distances are not reported because of the low accuracy of X-ray-determined proton positions; the $\alpha(O-H-O)$ angle, which is needed for E_{HB} (hydrogen bond energy) calculations, is reported for the cases in which its e.s.d. $\leq 2-4°$. In RAHBs the H-bond strength is known to be strictly related to the O=C–C=C–OH π delocalization;[2] this is measured by the antisymmetric stretching coordinate $Q = d_1 - d_4 + d_3 - d_2$ (**Ia**) or by the related coupling parameter $\lambda = (1 + Q/Q_0)/2$.[2b] In these compounds[5b] Q (λ) ranges from $Q = Q_0 = 0.320$ Å ($\lambda = 1.0$) to $Q = Q_0 = -0.320$ Å ($\lambda = 0$) for the totally π-localized keto–enol and enol–keto tautomers, respectively, including $Q = 0.0$ ($\lambda = 0.5$) for the totally π-delocalized form. Finally, hydrogen bond energies, E_{HB}, have been evaluated as a function of $d(O\cdots O)$ and $\alpha(O-H-O)$ by the Lippincott and Schroeder semiempirical formula.[6] For comparison, isolated nonresonant and noncooperative $O-H\cdots O$ bonds (vide infra) can be considered to have indicative ranges of $2.70 \leq d(O\cdots O) \leq 2.90$ Å, $3000 \leq \nu(O-H) \leq 3350\ \text{cm}^{-1}$ and $4.5 \geq E_{HB} \geq 1.5\ \text{kcal mol}^{-1}$.

Excluding compound **8**, whose hydrogen bond is weakened by bifurcation (Fig. 1), the data in Table 1 agree in indicating that the hydrogen bonds belonging to resonant β-chains are systematically shorter ($2.465 \leq d(O\cdots O) \leq 2.661$ Å) and more energetic ($15.5 \geq E_{HB} \geq 3.8\ \text{kcal mol}^{-1}$), and that their O–H bonds are weaker ($1200 \leq \nu(O-H) \leq 3030\ \text{cm}^{-1}$) than in the nonresonant case (e.g., 2.706 Å, 2.7 kcal mol^{-1} and 3270 cm^{-1} in the α-dimer **13**); moreover, β-diketone enols embedded in β-chains show an increased π-delocalization ($0.50 \leq \lambda \leq 0.80$; $0.0 \leq Q \leq 0.220$ Å), confirming the role played by resonance in strengthening the H-bond between conjugated neutral partners.[2]

The spread of values observed for geometrical, IR and energy parameters does not appear to depend in a systematic way on the type of β-chain formed but rather on chemical factors, in particular the nature of the heteroatom included in the cyclic pentane- or hexanedione group. In fact, the dispersion of data is considerably reduced by arranging the compounds in three groups: i) β-ketoesters (**1**, **10**, LASCAC10, IASCOR10) having $d(O\cdots O) = 2.605-2.661$ Å, $\nu(O-H) = 2800-3030\ \text{cm}^{-1}$, $E_{HB} = 6.3-3.8\ \text{kcal mol}^{-1}$, $\lambda = 0.73-0.88$; ii) simple β-diketones (**2**, **9**, PROLON, FACRIK, DIMEDO, JEMRAU) having $d(O\cdots O) = 2.539-2.625$ Å, $\nu(O-H) = 2500-3000\ \text{cm}^{-1}$, $E_{HB} = 9.7-6.5\ \text{kcal mol}^{-1}$, $\lambda = 0.50-0.77$; and iii) the single thiobarbituric acid derivative DETSBR01 with $d(O\cdots O) = 2.465$ Å, $\nu(O-H)$ ca. 1200 cm^{-1}, $E_{HB} = 15.5\ \text{kcal mol}^{-1}$ and $\lambda = 0.63$. The observed H-bond lengthening in β-ketoesters with respect to β-diketones is in agreement with that previously found for intramolecular H-bonds[2b, 2c] and is imputed to the hindering of the three-centre–four-electron bond because of the molecular asymmetry. The abnormally strong H-bond in DETSBR01 can be tentatively ascribed to increased π delocalizability of the β-diketone group induced by the fused thiourea moiety.

In **11** and **12** the hydrogen-bonded chains consist of enolone units interleaved with water molecules (Fig. 1). The single $O-H\cdots OH_2$ bond accepted by water is remarkably short (2.570 Å in **11** and 2.593 Å in **12**) while the two donated are longer (on average, 2.771 Å in **11** and 2.823 Å in **12**), the mean of both donated and accepted bonds being 2.704 and 2.746 Å in **11** and **12**, respectively. A similar bond pattern has been observed in α-oxalic acid dihydrate[11] where the two resonant O=C–OH groups make two independent chains intercalated by water molecules with $d(OH\cdots O_w) = 2.506$, mean $d(O_wH\cdots O) = 2.872$ and average $d(O\cdots O) = 2.750$ Å. In all three cases the average $d(O\cdots O)$ value along the chain (2.70–2.75 Å) is significantly longer than in resonant β-chains, suggesting that RAHB chaining is interrupted by the water molecules. The fact that the bond accepted by water is much shorter (0.25–0.30 Å) than the two bonds donated by it is more likely to result from a better balance of the repulsion and electronic forces in a situation in which there are different numbers of donors and acceptors (see Fig. 1).

Intercalated chains of resonant groups and water molecules can then be considered a case of inductive σ-bond cooperativity[12a] (as opposed to RAHB,[2a] or π-bond cooperativity[12a]), which is known to shorten slightly the $O\cdots O$ distance in $\cdots O-H\cdots O-H\cdots$ chains or rings of hydrogen-bonded waters and carboxylates or alcohols and phenols[13] with respect to the simple dimer. The most typical examples are phenols and alcohols, which form infinite chains of single donor–single acceptor $\cdots(R)O-H\cdots(R)O-H\cdots$ hydrogen bonds which are often remarkably short (e.g., $O\cdots O$ distances of 2.660, 2.671 and 2.65 Å in methanol,[13j] phenol[13f] and p-cresol,[13e] respectively). Similar patterns occur in the two ascorbic acid enantiomers LASCAC10 and IASCOR10 (Table 1), which, besides the β-chain, form other nonresonant chains through the α-hydroxyl groups; the average $d(O\cdots O)$ distances along the chain (2.742 and 2.732 Å) are in these cases means of two different values, 2.629 and 2.89 Å in the former and 2.587 and 2.89 Å in the latter. It seems evident that, because of the shallow energy-vs.-distance profile of H-bonding, many isoenergetic two-bond combinations are possible in slightly different steric fields but that the resultant cohesive energy can only be appreciated by averaging over the donated and accepted bonds.

Systematics of Strong $O-H\cdots O$ Bonds: With the aim of predicting the most probable hydrogen-bonded molecular patterns, it would be useful to group the great variety of intermolecular hydrogen bonds into chemical classes for which the relative ranges of hydrogen bond physical properties are known. This is done for the $O\cdots O$ contact distances in Figure 2, which summarizes data for the *intermolecular* $O-H\cdots O$ bonds among organic molecules obtained by merging the present results with those of a previous classification[2a] reporting $d(O\cdots O)$ intervals of 2.36–2.43 Å for (+)CAHBs ($=O\cdots H^+\cdots O=$ bonds in which a proton is captured by a pair of carbonyls, ether oxygens, water molecules or their combinations), 2.39–2.49 Å for (−)CAHBs ($-O-H\cdots {}^-O-$ bonds typically present in carboxylic acid–carboxylate pairs and in inorganic oxoacid salts), 2.46–2.65 and 2.55–2.69 Å for RAHBs in β-diketone and β-ketoester enols, respectively, and 2.62–2.70 Å for RAHB in carboxylic acids (both chains and dimers). Hydrogen bonds that are neither charged nor resonant are systematically longer ($d(O\cdots O) \geq 2.65$ Å); in Figure 2 they are divided in two subclasses called isolated or induction-assisted hydrogen bonds (IAHB)[14] according to whether they are simple dimeric associations or $\cdots OH\cdots OH\cdots$ chains, respectively. The slightly shorter $O\cdots O$ distances (2.65–2.75 Å) reported for IAHBs refer to averages between the H-bonds donated and accepted by the O–H group, and individual accepted bonds may sometimes be much shorter than this average (see previous section); isolated bonds were assigned the 2.77±0.07 Å range reported for polyalcohols and sugars.[15]

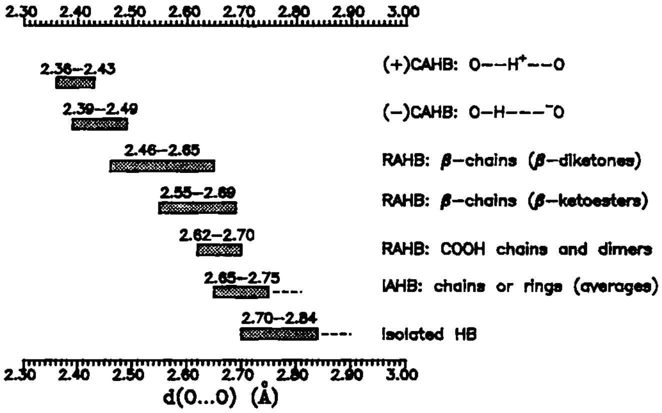


Fig. 2. Bar chart of the $d(O\cdots O)$ distances observed in organic crystals subdivided in chemical classes: (+ / −)CHAB = positive/negative-charge-assisted hydrogen bond; RAHB = resonance-assisted (or π-cooperative) hydrogen bond; IAHB induction-assisted (or σ-cooperative) hydrogen bond.

The $d(O\cdots O)$ ranges of Figure 2 can be transformed into intermolecular hydrogen bond energies, E_{HB}, by the Lippincott and Schroeder formula[6] by assuming a fixed $O-H\cdots O$ angle of 180°. The estimated E_{HB} values are 29.7–19.7 kcal mol^{-1} for (+)CAHBs, 25.2–13.4 for (−)CAHBs, 16.2–5.8 and 3.7–4.7 for RAHBs in β-diketones and β-ketoesters, respectively, 6.7–4.5 for RAHBs in carboxylic acids, 5.8–3.4 for IAHBs (on average) and 4.5–2.1 kcal mol^{-1} for isolated hydrogen bonds. These values are in reasonable agreement with the thermodynamic data available (7–8 kcal mol^{-1} for carboxylic acids,[16] 3.2–4.0 kcal mol^{-1} for nonresonant neutral bonds,[16d] 30–31 and 28 kcal mol^{-1}, respectively, for homomolecular (+)CAHBs and (−)CAHBs in the gas phase[17]) and with the most accurate theoretical calculations for RAHB.[18]

The last quantity considered is the IR $\nu(O-H)$ stretching frequency of the O–H bond. There are some useful relationships which link ν (or the stretching force constant $k = 4\pi^2\nu^2\mu$, where μ = reduced mass), the O–H dissociation energy D, bond distance d, and bond number n. They are the Pauling bond length–bond number formula (1),[19a] where $d(n)$ and

$$d(n) = d(1) - c\log_{10}n \qquad (1)$$

$d(1)$ = bond lengths for $n = n$ and 1, respectively, and c is a constant, the Johnston and Parr bond energy–bond order relationship (2)[19b] (p is a constant that assumes values $0.8 \leq p \leq 1.1$

$$D(n) = D(1)\, n^p \qquad (2)$$

for various types of bonds) and the empirical relationship (3).[19c] Bürgi and Dunitz have shown that all bonds whose

$$d = a - b\ln k \qquad (3)$$

energies can be expressed by a Morse equation conform to relationship (4), where A is a constant derivable from the Morse

$$4\pi^2\nu^2(n)\mu = k(n) = A\, n^p \qquad (4)$$

potential and p the same constant as in Equation (2).[19d] Then, if p is not far from unity, it would be expected that $\nu \propto k^{1/2} \propto n^{1/2}$. Moreover, the O–H bonds involved in hydrogen bonding must have $1 \geq n \geq 0.5$, and in this interval the approximations $n^{1/2} \propto n$ and, in Equation (1), $\log n \propto n$ probably lie within the dispersion of experimental data. In conclusion, a nearly linear dependence of ν(O–H) on n(O–H) and d(O–H) could be expected in hydrogen bonding studies, that is, Equation (5) applies.

$$\nu(\mathrm{O{-}H}) \propto n(\mathrm{O{-}H}) \propto d(\mathrm{O{-}H}) \qquad (5)$$

The ν(O–H) vs. d(O···O) plot of Figure 3a has been obtained by merging the data of Table 1 with others included by Novak in his 1974 review[7b] or retrieved from the more recent literature.[20] All data concern *intermolecular* O–H···O bonds with α(O–H–O) ≥ 165°; to increase the sample size, some inorganic oxoacids have also been included. Points are arranged on a smooth curve asymptotically approaching, on the upper right, the limiting frequency of ca. 3600 cm^{-1} for very long O···O distances and, on the lower left, the limiting O···O distance of some 2.40 Å for frequencies lower than 700 cm^{-1}. The distribution of chemical classes along this curve parallels that of the bar chart of Figure 2. The smallest distances and frequencies are associated with charged O–H···$^{-}$O bonds (○) and the largest ones with normal nonresonant O–H···O bonds (·: mostly waters of crystallization). Values for β-diketone enols (β-chains: □) are arranged in the middle of the curve together with those of other resonant systems (△: $HCrO_2$, Me_2AsOOH, H_2SO_4 and carboxylic acids). Finally, nonresonant σ-cooperative chains in ice, H_3BO_3, alcohols, phenols and carbohydrates, with (×) or without (+) water molecules, appear to be spread over most of the graph because they are often associations of short bonds accepted and long bonds donated by a single water or ROH moiety (vide supra).

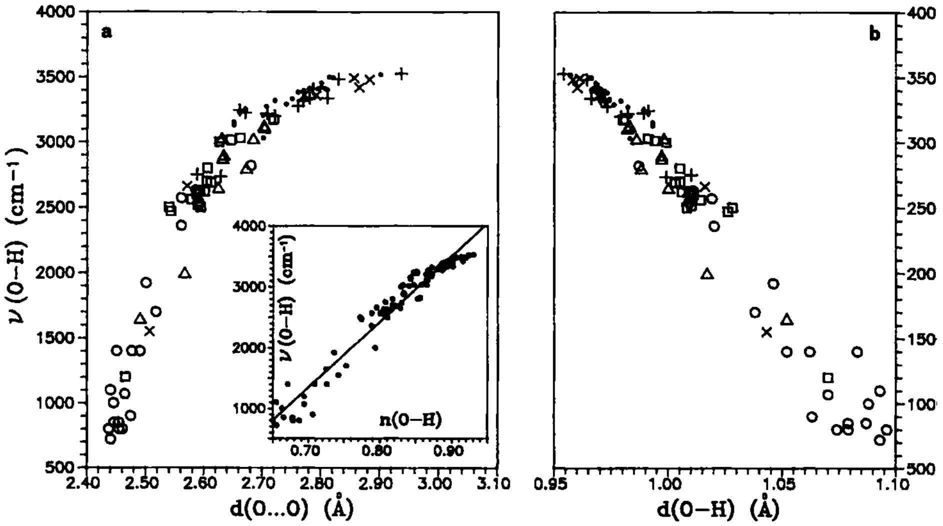


Fig. 3. a) ν(O–H) vs. d(O···O) scatter plot for a number of nearly linear intermolecular O–H···O hydrogen bonds observed in crystals. ○ = O–H···$^{-}$O; □ = resonant β-chains **Ia**; △ = other shorter resonant systems (carboxylic acids, $HCrO_2$, H_2SO_4, $(CH_3)_2As(O)OH$); + = cooperative ···OH···OH··· chains in ice, alcohols, phenols, H_3BO_3 and carbohydrates; × = water molecules intercalated in heteromolecular cooperative chains; · = nonresonant and noncooperative O–H···O bonds. *Inset*: ν(O–H) vs. n(O–H) (n = Pauling's bond order [19a]) scatterplot for the same data; b) ν(O–H) vs. d(O–H) for the same data as in a).

The linearization of the plot according to Equation (5) requires knowledge of d(O–H) and, from Equation (1), n(O–H). Though neutron structural data are presently unknown, both quantities can be calculated from the corresponding O···O distances through a previous correlation established for nearly linear intermolecular O–H···O bonds by the use of the best neutron data available.[21] In agreement with expectation and in spite of the approximations, both ν(O–H) vs. n(O–H) (inset in Fig. 3a) and ν(O–H) vs. d(O–H) (Fig. 3b) plots are essentially linear, with respective correlation coefficients $r = 0.975$ and 0.980. Figures 3a and 3b can be used to estimate the intermolecular O–H···O bond geometry from IR frequencies alone. For instance, a ν(O–H) of 2800 cm^{-1} would correspond to d(O–H) and d(O···O) values of about 1.00 and 2.62 Å, respectively.

Conclusions

The previous analysis performed on a large number of linear or nearly linear O–H···O intermolecular bonds shows that it is possible to establish a semiquantitative correspondence between d(O···O), ν(O–H) and d(O–H), on one side, and the bond energy, E_{HB}, on the other. Since E_{HB} rapidly decreases for O–H···O angles smaller than 165° but, at the same time, this angle becomes increasingly flat while E_{HB} increases, such a correspondence turns out to be the more accurate the stronger the H-bond is. More interestingly, the progressive decrease of E_{HB} can be associated with a hierarchy of chemical situations which are characterized by well-defined intervals of H-bond physical properties. In decreasing order of energy the most important are (+)CAHB (=O···H^{+}···O=), (−)CAHB (-O-H···$^{-}$O-), RAHB (β-diketones), RAHB (carboxylic acids) and, in reversed order, they can be assumed to direct the crystal packing process.

If our aim is to obtain crystals containing infinite hydrogen-bonded chains as a leitmotiv, the simplest way seems to be to choose molecules which are bifunctionalized on the opposite sites by the appropriate groups. For instance, bicarboxylic acids can be expected to aggregate in chains linked by carboxylic acid–carboxylate interactions ((−)CAHB) or carboxylic acid dimer formation (RAHB) according to whether they are crystallized from moderately basic or neutral solutions. The chains so obtained will be of little interest, however, because of the centrosymmetric (or apolar) distribution of the hydrogen bonds along the chain. The most interesting physical properties of the crystalline state require, in fact, chain polarity (e.g., pyro-, piezo- and ferroelectricity), a feature which can be easily obtained only by means of RAHB chains. In this case, β-diketone enols seem the most promising organic compounds to be investigated because they can be more easily synthesized than higher-order terms (such as ζ- and δ-diketone enols), form stronger H-bonds than carboxylic acids and, when included in a ring, can form only intermolecular bonds, which are most likely to develop β-chains as preferred structural patterns. In addition, such β-chains can be modulated in H-bond strength by a proper choice of the monomer (pure β-diketone or β-ketoester), as well as in shape by selecting the dimension of the ring (cyclopentane- or cyclohexanedione) and the steric characteristics of the substituents, as discussed in detail above. Finally, resonant β-chains are of intrinsic interest as prototypes of a class of switching-proton bistate molecular devices where the proton-transfer barrier is lowered by the RAHB mechanism and can accordingly be tuned at will by controlling the H-bond strength. Simple extension of RAHB to other heteroconjugated systems leads to other interesting compounds able to form resonant β-chains, for example enaminones $\cdots O{=}C{-}C{=}C{-}N(R)H\cdots$, which have been preliminarily examined in a recent study on the intermolecular $N{-}H\cdots O$ resonance-assisted hydrogen bond.[22]

Experimental Section

Crystal Structure Analysis: Compounds were purchased from Aldrich, except for **6** which was kindly provided by Drs. A. Barco and S. Benetti, University of Ferrara. The crystal structures of compounds **2** and **7** turned out to have been previously determined by Katrusiak [8a,b]; our results were retained for the sake of uniformity. All X-ray diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) and $\omega/2\theta$ scan technique ($2 \leq \theta \leq 28°$). Lattice constants were determined by least-squares fitting of the setting angles of 25 reflections in the range $10 \leq \theta \leq 14°$. Intensities of three standard reflections were measured every 2 h and did not show significant variations for any of the compounds investigated. Intensities were corrected for Lorentz and polarization effects. Scattering factors were taken from ref. [23]. Structures were solved by direct methods with the SIR88 package [24a]. Calculations were accomplished by the MolEN package [24b] and PARST [24c]. Structural references were mostly taken from the Cambridge Structural Database (CSD) [5a].

Crystal Data for 1: 4-Hydroxy-3-phenyl-2(5*H*)-furanone, $C_{10}H_8O_3$, triclinic $P\bar{1}$ (no. 2), $a = 9.675(2)$, $b = 12.350(2)$, $c = 7.493(2)$ Å, $\alpha = 95.78(2)$, $\beta = 111.67(2)$, $\gamma = 85.21(1)°$, $V = 826.8(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.42$ gcm^{-3}, $\mu = 0.98$ cm^{-1}. Of the 3968 unique measured reflections, 2230 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.051, $R_w = 0.064$.

Crystal Data for 2: 2-Methyl-1,3-cyclohexanedione, $C_7H_{10}O_2$, orthorhombic *Ibam* (no. 72), $a = 13.708(1)$, $b = 13.556(1)$, $c = 7.188(1)$ Å, $V = 1336.7(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.25$ gcm^{-3}, $\mu = 0.85$ cm^{-1}. Of the 873 unique measured reflections, 556 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.050, $R_w = 0.070$.

Crystal Data for 3: 5-Methyl-1,3-cyclohexanedione, $C_7H_{10}O_2$, orthorhombic $Cmc2_1$ (no. 36), $a = 6.895(1)$, $b = 11.576(3)$, $c = 9.141(6)$ Å, $V = 729.6(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.15$ gcm^{-3}, $\mu = 0.78$ cm^{-1}. Of the 600 unique measured reflections, 264 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.075, $R_w = 0.106$.

Crystal Data for 4: Ethyl-4-hydroxy-6-methyl-2-oxo-3-cyclohexene-1-carboxylate, $C_{10}H_{14}O_4$, monoclinic $P2_1/c$ (no. 14), $a = 9.855(2)$, $b = 10.636(2)$, $c = 10.242(2)$ Å, $\beta = 105.57(2)°$, $V = 1034.2(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.27$ gcm^{-3}, $\mu = 0.92$ cm^{-1}. Of the 2483 unique measured reflections, 1085 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.056, $R_w = 0.063$.

Crystal Data for 5: 6,6-Dimethyl-1,3-cyclohexanedione, $C_8H_{12}O_2$, orthorhombic $P2_12_12_1$ (no. 19), $a = 6.701(2)$, $b = 9.370(1)$, $c = 12.899(2)$ Å, $V = 809.9(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.15$ gcm^{-3}, $\mu = 0.76$ cm^{-1}. Of the 1148 unique measured reflections, 663 with $I \geq 2\sigma(I)$ were used in the refinement. R (on F) = 0.057, $R_w = 0.078$.

Crystal Data for 6: 2,2′-Ethylene bis(1,3-cyclohexanedione), $C_{14}H_{18}O_4$, monoclinic $P2_1/n$ (no. 14), $a = 8.149(2)$, $b = 12.224(2)$, $c = 12.633(2)$ Å, $\beta = 94.74(2)°$, $V = 1254.2(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.33$ gcm^{-3}, $\mu = 0.90$ cm^{-1}. Of the 3020 unique measured reflections, 1888 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.041, $R_w = 0.048$.

Crystal Data for 7: 2-Methyl-1,3-cyclopentanedione, $C_6H_8O_2$, monoclinic $C2/m$ (no. 12), $a = 12.770(2)$, $b = 6.808(1)$, $c = 6.476(1)$ Å, $\beta = 93.95(1)°$, $V = 561.7(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.33$ gcm^{-3}, $\mu = 0.93$ cm^{-1}. Of the 883 unique measured reflections, 685 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.048, $R_w = 0.069$.

Crystal Data for 8: 2-Hydroxy-1,4-naphthoquinone, $C_{10}H_6O_3$, triclinic $P\bar{1}$ (no. 2), $a = 9.526(2)$, $b = 12.298(2)$, $c = 7.122(1)$ Å, $\alpha = 104.58(2)$, $\beta = 103.43(2)$, $\gamma = 82.03(2)°$, $V = 782.6(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.48$ gcm^{-3}, $\mu = 1.03$ cm^{-1}. Of the 3764 unique measured reflections, 2417 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.039, $R_w = 0.053$.

Crystal Data for 9: 5,5-Dimethyl-2-chloro-1,3-cyclohexanedione, $C_8H_{11}ClO_2$, monoclinic $P2_1/c$ (no. 14), $a = 6.592(2)$, $b = 11.294(3)$, $c = 11.908(4)$ Å, $\beta = 99.13(1)°$, $V = 875.3(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.33$ gcm^{-3}, $\mu = 3.83$ cm^{-1}. Of the 2104 unique measured reflections, 331 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.050, $R_w = 0.054$.

Crystal Data for 10: 4-Hydroxy-6-methyl-2-pyrone, $C_6H_6O_3$, monoclinic $P2_1/n$ (no. 14), $a = 3.895(1)$, $b = 16.447(1)$, $c = 9.255(1)$ Å, $\beta = 99.94(2)°$, $V = 584.0(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.44$ gcm^{-3}, $\mu = 1.09$ cm^{-1}. Of the 1392 unique measured reflections, 994 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.037, $R_w = 0.055$.

Crystal Data for 11: 4-Hydroxycoumarin monohydrate, $C_9H_6O_3 \cdot H_2O$, orthorhombic $P2_12_12_1$ (no. 19), $a = 6.922(1)$, $b = 10.044(1)$, $c = 12.144(1)$ Å, $V = 844.3(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.42$ gcm^{-3}, $\mu = 1.06$ cm^{-1}. Of the 1190 unique measured reflections, 827 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.034, $R_w = 0.045$.

Crystal Data for 12: 4-Hydroxy-5-methyl-4-cyclopentene-1,3-dione monohydrate, $C_6H_6O_3 \cdot H_2O$, monoclinic $P2_1/n$ (no. 14), $a = 5.241(2)$, $b = 19.121(3)$, $c = 6.899(1)$ Å, $\beta = 93.96(2)°$, $V = 689.7(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.39$ gcm^{-3}, $\mu = 1.11$ cm^{-1}. Of the 1603 unique measured reflections, 1010 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.050, $R_w = 0.064$.

Crystal Data for 13: 4-Hydroxy-5-phenyl-4-cyclopentene-1,3-dione, $C_{11}H_8O_3$, monoclinic $P2_1/c$ (no. 14), $a = 5.255(1)$, $b = 10.550(1)$, $c = 15.881(2)$ Å, $\beta = 99.16(2)°$, $V = 869.2(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.44$ gcm^{-3}, $\mu = 0.98$ cm^{-1}. Of the 2080 unique measured reflections, 1436 with $I \geq 3\sigma(I)$ were used in the refinement. R (on F) = 0.038, $R_w = 0.049$.

Structures were refined by full-matrix least squares. For **1**, **4**, **6–8** and **10–13** the refinement was anisotropic for non-H and isotropic for H atoms. In **6** the two enolic protons were also refined anisotropically, as illustrated in Figure 1. The molecules of **2** and **3** lie on a crystallographic mirror with the β-diketone moiety on the plane and the remaining atoms disordered over two symmetric positions around the mirror. A similar disorder is observed in compound **5** with the difference that the molecules occupy general positions. In all cases non-H atoms were refined anisotropically with disordered atoms in general positions and 0.5 occupancy; hydrogen atoms were refined isotropically in **2** and **3** and kept in fixed positions in **5** (except the enolic H(1) proton refined isotropically). Compound **9** was refined with anisotropic non-H atoms and hydrogens in calculated fixed positions; the enolic H(3) atom was located from ΔF. Figure 1 shows ORTEP [24d] views of the molecules and PLUTO [24e] drawings of their hydrogen bond patterns. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-1220-14. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk) [20].

IR Spectroscopic Data: IR spectra for **1–13** and for a number of similar compounds of known crystal structure commercially obtainable were recorded on a Nicolet 510P FTIR spectrometer in KBr with a diffuse reflectance accessory. Measured and literature [7e–g] values of ν(O–H) stretching frequencies and their assignements to specific O–H···O bonds are given in Table 1 [20].

Acknowledgments: Financial support for this work from the Italian Ministry for the University and Scientific and Technological Research (MURST, Rome) is gratefully acknowledged.

Received: December 12, 1995 [F266]

---

[1] a) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, **1989**; b) P. Hartman, W. G. Perdok, *Acta Crystallogr.* **1959**, *8*, 49, 521; P. Hartman, *ibid.* **1959**, *12*, 432; c) A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, **1973**.

[2] a) P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* **1994**, *116*, 909; b) G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, *ibid.* **1989**, *111*, 1023; c) V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, *ibid.* **1991**, *113*, 4917; d) G. Gilli, V. Bertolasi, V. Ferretti, P. Gilli, *Acta Crystallogr. Sect. B* **1993**, *49*, 564; e) G. Gilli, V. Bertolasi, in *The Chemistry of Enols* (Ed.: Z. Rappoport), Wiley, New York, **1990**, ch. 13; f) P. Gilli, V. Ferretti, V. Bertolasi, G. Gilli, *A Novel Approach to Hydrogen Bonding Theory* in *Advances in Molecular Structure Research, Vol. 2* (Eds.: M. Hargittai, I. Hargittai), JAI Press, Greenwich, CT, **1996**, pp. 67–102.

[3] a) F. R. Thornley, R. J. Nelmes, K. D. Rouse, *Chem. Phys. Lett.* **1975**, *34*, 175; b) Z. Tun, R. J. Nelmes, W. F. Kuhs, R. F. D. Stansfield, *J. Phys. C: Solid State Phys.* **1988**, *21*, 245; c) A. L. MacDonald, J. C. Speakman, D. Hadzi, *J. Chem. Soc. Perkin Trans. 2* **1972**, 825; d) A. McAdam, M. Currie, J. C. Speakman, *J. Chem. Soc.* **1971**, 1994.

[4] a) D. S. Chemla, J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals, Vols. 1, 2*, Academic Press, Orlando, **1987**; b) P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, **1991**.

[5] a) F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers, D. G. Watson, *Acta Crystallogr. Sect. B* **1979**, *35*, 2331; b) F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. II* **1987**, S1; c) W. Klyne, V. Prelog, *Experientia* **1960**, *16*, 521.

[6] a) E. R. Lippincott, R. Schroeder, *J. Chem. Phys.* **1955**, *23*, 1099; b) R. Schroeder, E. R. Lippincott, *J. Phys. Chem.* **1957**, *61*, 921.

[7] a) J. Emsley, *Struct. Bonding* **1984**, *57*, 147; b) A. Novak, *ibid.* **1974**, *18*, 177; c) T. S. Kopteva, D. N. Shigorin, *Russ. J. Phys. Chem.* **1974**, *48*, 312; d) *The Hydrogen Bond, Vol. 2* (Eds.: P. Schuster, G. Zundel, C. Sandorfy), North Holland, Amsterdam, **1976**, ch. 12–18; e) G. Kirsch, J. L. Mieloszynsky, D. Paquer, C. G. Andrieu, *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 489; f) D. W. Schiering, J. E. Katon, *Appl. Spectrosc.* **1986**, *40*, 1049; g) J.-P. Bideau, P. V. Huong, S. Toure, *Acta Crystallogr. Sect. B* **1976**, *32*, 481.

[8] a) A. Katrusiak, *J. Cryst. Spectr. Res.* **1993**, *23*, 367; b) A. Katrusiak, *Acta Crystallogr. Sect. C* **1989**, *45*, 1897; c) D. Semmingsen, *Acta Chem. Scand. Ser. B* **1977**, *31*, 114; d) M. C. Etter, Z. Urbanczyk-Lipkowska, D. A. Jahn, J. S. Frye, *J. Am. Chem. Soc.* **1986**, *108*, 5871; e) J.-P. Bideau, G. Bravic, A. Filhol, *Acta Crystallogr Sect. B* **1977**, *33*, 3847; f) D. Semmingsen, *Acta Chem. Scand. Ser. B* **1974**, *28*, 169; g) A. Katrusiak, *Acta Crystallogr. Sect. C* **1990**, *46*, 1289; h) J. Hvoslef, *Acta Crystallogr. Sect. B* **1968**, *24*, 1431; i) N. Azarnia, H. M. Berman, R. D. Rosenstein, R. D. *ibid.* **1971**, *27*, 2157; j) M. S. Chambers, E. J. Thomas, D. J. Williams, *J. Chem. Soc. Chem. Commun.* **1987**, 1228; k) P. de Meester, M. V. Jovanovich, S. S. C. Chu, E. R. Biehl, *J. Heterocycl. Chem.* **1986**, *23*, 337; l) K. H. Schönwälder, P. Kollat, J. J. Stezowski, F. Effenberger, *Chem. Ber.* **1984**, *117*, 3280; m) E. Gavuzzo, F. Mazza, A. Carotti, G. Casini, *Acta Crystallogr. Sect. C* **1984**, *40*, 1231; n) L. Trifonov, J. H. Bieri, R. Prewo, A. S. Dreiding, D. M. Rast, L. Hoesch, *Tetrahedron* **1982**, *38*, 397; o) E. Krogh Andersen, I. G. Krogh Andersen, *Acta Crystallogr. Sect. B* **1975**, *31*, 394; p) E. Krogh Andersen, I. G. Krogh Andersen, G. Ploug-Sørensen, *Acta Chem. Scand. Ser. A* **1987**, *41*, 213; q) D. Semmingsen, F. J. Hollander, T. F. Koetzle, *J. Chem. Phys.* **1977**, *66*, 4405.

[9] a) P. Murray-Rust, J. P. Glusker, *J. Am. Chem. Soc.* **1984**, *106*, 1018; b) J. P. Glusker, M. Lewis, M. Rossi, *Crystal Structure Analysis for Chemists and Biologists*, VCH, New York, **1994**, ch. 17.

[10] a) R. Chidambaram, S. K. Sikka, *Chem. Phys. Lett.* **1968**, *2*, 162; b) T. Steiner, W. Saenger, *Acta Crystallogr. Sect. B* **1992**, *48*, 819; c) T. Steiner, W. Saenger, *ibid.* **1994**, *50*, 348.

[11] a) T. M. Sabine, G. W. Cox, B. M. Craven, *Acta Crystallogr. Sect. B* **1969**, *25*, 2437; b) R. G. Delaplane, J. A. Ibers, *ibid.* **1969**, *25*, 2423.

[12] a) G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, **1991**, p. 35; b) G. A. Jeffrey, M. E. Gress, S. Takagi, *J. Am. Chem. Soc.* **1977**, *99*, 609; c) G. A. Jeffrey, L. Lewis, *Carbohydr. Res.* **1978**, *60*, 179; d) Y. C. Tse, M. D. Newton, *J. Am. Chem. Soc.* **1977**, *99*, 611; e) T. Steiner, S. A. Mason, W. Saenger, *ibid.* **1990**, *112*, 6184; f) T. Steiner, W. Saenger, *ibid.* **1992**, *114*, 7123; g) G. A. Jeffrey, *Cryst. Rev.* **1995**, *4*, 213.

[13] a) A. Thozet, M. Perrin, *Acta Crystallogr. Sect. B* **1980**, *36*, 1444; b) J. C. A. Boeyens, J. A. Pretorius, *ibid.* **1977**, *33*, 2120; c) M. T. Vandenborre, H. Gillier-Pandraud, D. Antona, P. Becker, *ibid.* **1973**, *29*, 2488; d) C. Bois, *ibid.* **1970**, *26*, 2086; e) M. Perrin, A. Thozet, *Cryst. Struct. Comm.* **1974**, *3*, 661; f) V. E. Zavodnik, V. K. Bel'skii, P. M. Zorkii, *Zh. Strukt. Khim.* **1987**, *28*, 175; g) C. Bavoux, A. Thozet, *Acta Crystallogr. Sect. B* **1973**, *29*, 2603; h) C. Bois, *ibid.* **1973**, *29*, 1011; i) R. Perrin, M. Lamartine, M. Perrin, A. Thozet in *Organic Solid State Chemistry* (Ed.: G. R. Desiraju), Elsevier, Amsterdam, **1987**, ch. 8; j) K. J. Tauer, W. N. Lipscomb, *Acta Crystallogr.* **1952**, *5*, 606.

[14] With the discovery of ever more classes of H-bonds the nomenclature is becoming increasingly confused. A complete (we hope) list of correspondence is: a) positive charge-assisted H-bonds, (+)CAHB (ref. [2d]); b) negative charge-assisted H-bonds, (−)CAHB (ref. [2d]), also called salt bridges in inorganic chemistry; c) resonance-assisted hydrogen bonds, RAHB (ref. [2b]), also called π-cooperative H-bonds (ref. [12a]); d) induction-assisted H-bond, IAHB, also called σ-cooperative (ref. [12a]) or polarization-assisted H-bonds (ref. [12g]); and e) isolated (i.e., noncharged and noncooperative) H-bonds. In view of the σ/π separability, we suggest use of polarization-assisted H-bond (PAHB) as a general definition that encompasses both RAHB (π-cooperative) and IAHB (σ-cooperative).

[15] a) J. Kroon, J. A. Kanters, J. G. C. M. Van Duijneveldt-Van de Rijdt, F. B. Van Duijneveldt, J. A. Vliegenthart, *J. Mol. Struct.* **1975**, *24*, 109; b) C. Ceccarelli, G. A. Jeffrey, R. Taylor, *ibid.* **1981**, *70*, 255.

[16] a) C. H. D. Calis-van Ginkel, G. H. M. Calis, C. W. M. Timmermans, C. G. de Kruif, H. A. J. Oonk, *J. Chem. Thermodynamics* **1978**, *10*, 1083; b) J. Chao, B. J. Zwolinski, *J. Phys. Chem. Ref. Data* **1978**, *7*, 363; c) S. Murata, M. Sakiyama, J. Seki, *J. Chem. Thermodynamics* **1982**, *10*, 14, 723; d) L. A. Curtiss, M. Blander, *Chem. Rev.* **1988**, *88*, 827.

[17] a) M. Meot-Ner (Mautner), *J. Am. Chem. Soc.* **1984**, *106*, 1257; b) M. Meot-Ner (Mautner), L. W. Siek, *ibid.* **1986**, *108*, 7525; c) M. Meot-Ner (Mautner), in *Molecular Structure and Energetics, Vol. IV* (Eds.: J. F. Liebman, A. Greenberg) VCH, Weinheim, **1987**, ch. 3.

[18] a) M. J. Frisch, A. C. Scheiner, H. F. Schaefer III, J. S. Binkley, *J. Chem. Phys.* **1985**, *82*, 4194; b) L. Turi, J. J. Dannenberg, *ibid.* **1992**, *96*, 5819; c) L. Turi, J. J. Dannenberg, *Chem. Mater.* **1994**, *6*, 1313; d) J. J. Dannenberg, R. Rios, *J. Phys. Chem.* **1994**, *98*, 6714.

[19] a) L. Pauling, *J. Am. Chem. Soc.* **1947**, *69*, 542; b) H. S. Johnston, *Adv. Chem. Phys.* **1960**, *3*, 131, and H. S. Johnston, C. Parr, *J. Am. Chem. Soc.* **1963**, *85*, 2544; c) D. R. Herschbach, V. W. Laurie, *J. Chem. Phys.* **1961**, *35*, 458, and H. S. Johnston, *J. Am. Chem. Soc.* **1964**, *86*, 1643; d) H.-B. Bürgi, J. D. Dunitz, *J. Am. Chem. Soc.* **1987**, *109*, 2924; e) H.-B. Bürgi, *Inorg. Chem.* **1973**, *12*, 2321; f) H.-B. Bürgi, *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 460.

[20] Additional material available from the authors on request: a) full list of structural and spectroscopic data used in Figure 3; b) chemical formulae of all compounds of Table 2 classed according to Scheme 3.

[21] Symmetrical three-centre–four-electron bonds such as O·–·H···:O follow the bond order conservation rule $n_1 + n_2 = 1$ (ref. [19b,e,f]), where n_1 and n_2 are the bond numbers of the O–H and H···O bonds and n is defined by Pauling's formula $\Delta d = -c\log_{10}n$ (ref. [19a]). It can be shown (ref. [2a]) that for *nearly linear* bonds, $r^* - r^o = -c\log_{10}(1 - 10^{-(r-r^o)/c})$ and $R = r + r^*$, where $r = d(\mathrm{O{-}H})$, $r^* = d(\mathrm{H\cdots O})$, $R = d(\mathrm{O\cdots O})$, $r^o = d(\mathrm{O{-}H})$ in the absence of hydrogen bonding and $c = [R_{min}/2 - r^o]/\log_{10}2$, R_{min} being the shortest $d(\mathrm{O\cdots O})$ value observable. The best fit is obtained for $R = 2.40$, $r^o = 0.925$ and $c = 0.9135$ Å. From these equations $r = d(\mathrm{O{-}H})$ can be obtained from $R = d(\mathrm{O\cdots O})$; finally, the relationship $r = d(\mathrm{O{-}H}) = 0.925 - 0.9135 \log_{10}n(\mathrm{O{-}H})$ makes it possible to calculate the bond order of the O–H bond.

[22] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, *Acta Crystallogr. Sect. B* **1995**, *51*, 1004.

[23] *International Tables for X-Ray Crystallography, Vol. 4*, Kynoch Press, Birmingham, **1974**, p. 71.

[24] a) M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D. Viterbo, *SIR88. A Direct-Methods Program for the Automatic Solution of Crystal Structures*, *J. Appl. Crystallogr.* **1989**, *22*, 389; b) *MolEN. An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, NL, **1990**; c) M. Nardelli, *Comput. Chem.* **1983**, *7*, 95; d) C. K. Johnson, *ORTEP II: A Fortran Thermal Ellipsoids Plot Program for Crystal Structure Illustrations*, Report ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, **1976**; e) W. D. S. Motherwell, W. Clegg, *PLUTO Program for Plotting Molecular and Crystal Structures*, University of Cambridge (UK), **1978**.